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Silicones

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I. INTRODUCTION

Silicones are a broad family of synthetic polymers that are partly inorganic and partly organic. Their structure consists of alternating silicon and oxygen atoms rather than the carbon-to-carbon backbone that characterizes organic materials. Typically, one or more organic side groups are attached to the silicon atoms, imparting properties such as chemical resistance, lubricity, improved thermal and oxidative stability, and reactivity with organic chemicals and polymers. Additionally, these materials are characterized by chemical inertness, low surface tension, excellent water repellency, good electrical properties and weatherability, and a high degree of slip on most rubber or plastic surfaces.

Silicones are grouped into three major categories: fluids, resins, and elastomers (Fig. 1).

Silicone fluids in commercial use often have side groups such as methyl, trifluoropropyl, phenyl, vinyl, longer alkyl, and other organic groups. In addition, they may be modified with the use of fillers, solvents, antioxidants, or lubricity additives for use in a wide variety of applications.

II. HISTORICAL DEVELOPMENT

Organosilicone chemistry had its beginnings about 100 years ago. Kipping of England was the first to name silicones. As early as 1904, he synthesized a number of R—Si—X compounds using Grignard reagents. As scientific knowledge about the formation of large polymer molecules increased in the early 1930s, industrial development of silicones began [1].

Early work focused on resinous polymers for use as insulating materials that would withstand temperatures above the 105°C limit of class A insulation [2], In 1940, through research done at its corporate research and development laboratory in Schenectady, New York, General Electric became the first company to successfully develop an economical procedure for silicone production. Both Dow Corning Corporation and General Electric began commercial development of silicone polymers during the 1940s. The Dow Corning plant opened in 1943; General

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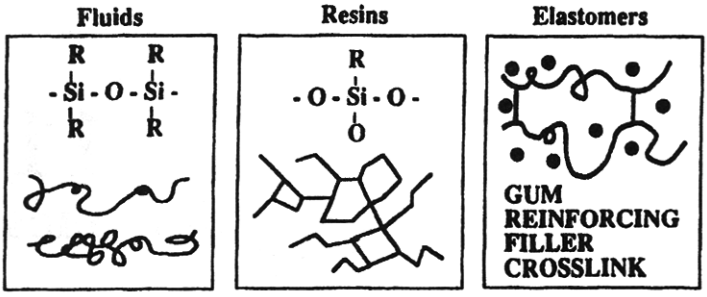

Figure 1 The three major categories of silicones.

Electric began commercial production in 1944 and completed the initial phase of its Waterford facility in 1947.

Silicones were initially used for military applications during World War II, followed by use in the aerospace industry. Silicones' success in meeting the demanding environmental conditions characteristic of these applications, together with their thermal and chemical stability, led to increased usage in the United States.

Typical military applications for silicones include damping fluids for aircraft instruments, antifoams in petroleum oils, and greases used as ignition sealing compounds. After World War II, civilian uses expanded beyond these applications to include release agents for molding rubber, water repellents, and ingredients for paints, lubricants, and polishes.

In recent years, silicones have grown from a chemical rarity into a widely used family of products. Silicone fluids have proved extremely versatile in solving many industrial problems and have been key ingredients in a number of new products. Probably no other synthetic fluid has found such a variety of uses in so many different industries.

III. CHEMISTRY

A. Product Structure

Silicone fluids are unique polymers that combine an inorganic silicon–oxygen (siloxane) backbone with organic side chains: R groups such as methyl (CH_3) and phenyl (C_6H_5), as shown in Fig. 2. This hybrid nature explains why silicones behave somewhat like organic polymers, yet retain important inorganic properties like heat resistance.

Many of the unique properties of silicone fluids are due to the free rotation of molecules along the Si—O and Si—C bond axes and the flexible nature of the siloxane backbone. This freedom of motion leads to greater intermolecular distance and, therefore, to lower intermolecu-lar

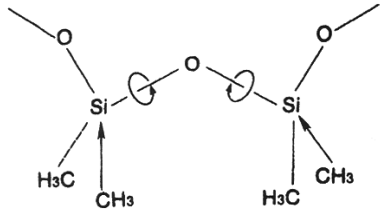

Figure 2 The hybrid nature of the silicone polymer.

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forces. These factors explain the low modulus, low glass transition temperatures (T_g), and high permeability of silicones [3].

Structure also explains the slight temperature dependence of other properties, such as viscosity. At lower temperatures, the siloxane has short chain extension and low molecular entanglement of the R groups. As the chain extends with higher temperatures, the backbone must shift to a higher energy configuration where the R groups are closer together. The greater molecular mobility due to temperature is thus negated by increased molecular entanglement. Therefore, the viscosity of the flexible silicone has much less temperature dependence that does the stiff-chained hydrocarbon [5].

B. Nomenclature

Silicone terminology is a blend of "official" International Union of Pure and Applied chemistry (IUPAC) rules, American Chemical Society (ACS) rules, and commonly used shorthand.

The terminology borrows from organic chemistry nomenclature and defines SiH_4 as silane, analogous to CH_4, methane. Hence, H_3SiCl is cholorosilane; $(CH_3)_2SiCl_2$ is dimethyldichlorosilane; and H_3SiOH is silanol. The molecule $H_3SiOSiH_3$ is disiloxane; polymers are polyorganosiloxanes (a more descriptive term than silicone). Polydimethylsiloxanes (PDMS) are the predominant commercial polymers.

Strictly proper nomenclature can be awkward to use, especially with polymer chemistry and in the spoken language. A useful shorthand has been developed, and it reflects the predominance of PDMS polymers. The letters M, D, T, and Q are used to represent mono-, di-, tri-, and quadrifunctional monomer units: that is, monomer units with the silicon bonded to one, two, three, and four oxygen atoms, respectively. (Keep in mind that each O is actually a bridge in the siloxane chain and is "shared" by two Si atoms.) The remaining substituents are labeled with a prime, such as M′ [3]. Table 1 and 2 show common examples of this nomenclature and other common shorthand terms.

The D-chain-propagating units are used to build up the polymer, since they can form one Si—O bond to the growing chain and still have a bond site available to add the next monomer unit. The M units are used as chain terminators, since simply attaching to the chain uses their only Si—O bond site. The T and Q units are used to add branching and cross-linking, especially in resins.

C. Synthetic Methods

Oxygen (50%) and silicon (25%) are the most abundant elements in the earth's crust. Silicon is not found pure in nature, but rather in combination with oxygen in a wide variety of three-dimensional crystalline networks called silicates (Fig. 3).

The substitution of atoms such as iron, aluminum, calcium, sodium, and potassium in the matrix gives rises to a wide variety of rocks and minerals. Through the craft of ceramics, humans have been using practical silicate chemistry for thousands of years [6,7]. Because of the stable nature of silicates, however, silicon was not isolated and recognized as an element until 1824.

Since silicon and carbon are both tetravalent (have four bonding electrons available), much of the research in the 1800s focused on synthesizing silicon analogues of organic compounds (Figs. 4 and 5).

However, there was little success. Silicon's more complex electron orbital structure causes silicon chemistry to differ from carbon (organic) chemistry in several important ways [6,7]:

1. Si—Si and Si—H bonds react rapidly with oxygen and water, making them unstable under normal conditions (they will react with air).

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Table 1 Siloxane Structures

Chemical name	Structural formula	MDT formula	Common name
Hexamethyldisiloxane	$(CH_3)_3SiOSi(CH_3)_3$	MM	Mono
Octamethyltrisiloxane	$(CH_3)_3SiOSi(CH_3)_2)Si(CH_3)_3$	MDM	Linear trimer
Decamethyltertrasiloxane	$(CH_3)SiO]Si(CH_3)_2O]Si(CH_3)_3$	MD_2M	Linear tetramer
Octamethylcyclotetrasiloxane	$(CH_3)_2Si$---O---$Si(CH_3)_2$ O O $(CH_3)_2Si$----O---$Si(CH_3)_2$		
Octaphenylcyclotetrasiloxane	$C_6H5)_2Si$---)---$Si(C_6H_5)_2$ O O $(C_6H_5)_2Si$---O---$Si(C_6H_5)_2$	D'_4	Cyclic phenyltetramer
2,4,6,8-Tetramethyl-2,4,6,8-tetraphenly-cyclotetrasiloxane	$(CH_3)(C_6H_5)Si$---O---$Si(CH_3)(C_6H_5)$ O O $(CH_3)(C_6H_5)Si$---O---$Si(CH_3)(C_6H_5)$	D'_4	Cyclic methylpheny-tetramer
Methyltris (trimethylsiloxy) silane	$[(CH_3)_3SiO]_3SiCH_3$	M_3T	
1,1,1,3,5,5,5,-Heptamethytri-siloxane	$(CH_3)_3SiOSi(H)(CH_3)Osi(CH_3)_3$	MD'M	
1,1,3,5,5-Pentamethyl-1,3,5-triphenyltrisiloxane	$(CH_3)_2(C_6H_5)SiOSi(CH_3)C_6H_5)$ $Osi(C_6H_5)(CH_3)_2$	M'D'M'	

Table 2 Silicone Functionality: Shorthand Notation

Formula	Functionality	Symbol
$(CH_3)_3SiO_{0.5}$	Mono	M
$(CH_3)_2SiO$	Di	D
$(CH_3)SiO_{1.5}$	Tri	T
$(CH_3)(C_6H_5)SiO$	Di	D′
$(C_6H_5)_2SiO$	Di	D′
$(CH_3)(H)SiO$	Di	D′
SiO_2	quadri	Q

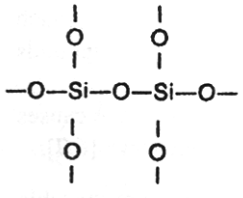

Figure 3 Structure of the silicate network.

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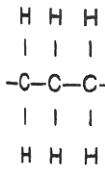

Figure 4 Carbon bonding.

2. Silicone has a tremendous affinity for (and is difficult to separate from) oxygen. Put another way, silicon builds polymers with oxygen, while oxygen tends to degrade hydrocarbons to single molecules ($C0_2$ and CO).
3. Silicon does not form double bonds, while C═C and C═O bonds are important in organic chemistry.
4. Silicon compounds generally require higher energy (higher temperature) to react, making them more stable.

The potential usefulness of the Si—O bond was not realized until the 1930s, when organic resins used for electrical insulation were found to be inadequate for new higher temperature applications. It was thought that a resin siloxane backbone with small organic side chains might have the proper temperature resistance [5].

Early synthetic schemes used Grignard reagents and silicon tetrachloride. The Grignard reagents is prepared as follows:

$$Mg + RBr \rightarrow RMgBr$$

The silicon tetrachloride is derived from quartzite rock, oil coke (carbon), and chlorine gas:

$$SiO_2 + 2C \rightarrow Si + 2CO \text{ (electric furnace)}$$
$$Si + 2Cl_2 + \text{heat} \rightarrow SiCl_4$$

The reactants are combined in the presence of ether as follows:

$$2RMgBr + SiCl_4 \rightarrow R_2SiCl_2 + 2MgBrCl$$
$$nR_2SiCl_2 + (2n)H_2O \rightarrow (2n)HCl + nR_2Si(OH)_2$$
$$nR_2Si(OH)_2 \rightarrow nH_2) + (R_2SiO)_n \text{ (linear and cyclic)}$$

This method proved costly and difficult on a production scale. Safety is also a concern with large quantities of reactive materials such as ether and magnesium.

A direct process involving a catalyst was developed by Rochow of General Electric Company that allowed the chlorosilane intermediates to be produced in one step:

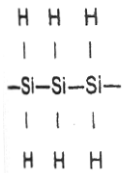

Figure 5 Polysilane.

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$$Si + 2RCl \xrightarrow{cat} R_2SiCl_2$$

$$nR_2SiCl_2 + (2n)H_2O \rightarrow (2n)HCl + nR_2Si(OH)_2$$

$$nR_2Si(OH)_2 \rightarrow nH_2O + R_2SiO)_n \text{ (linear and cyclic)}$$

This process made the commercialization of silicones possible, and it remains the standard of the industry.

D. Current Commercial Routes

Commercial silicone manufacture starts with the production of chlorosilane intermediates, especially methylchlorosilanes.

Typically, methyl chloride vapor is passed at high velocity through a fluid-bed reactor containing finely ground silicon metal and copper catalyst. The silicon is converted (at up to 90% efficiency) to a crude mix of dimethyldichloro-, methyltrichloro-, dimethyldichloro-, and trimethylchlorosilanes, as well as other monosilanes and higher boiling residues [3] (Fig. 6). Conditions are generally set to yield at least 50% dimethyldichlorosilanes.

Fractional distillation columns are used to separate the desired components from the crude mix. The task is somewhat difficult, since the boiling points of the chlorosilanes are similar (Table 3).

Methylchlorosilanes are converted to silicone fluids in a two-step process. In the hydrolysis step, dimethyldichlorosilane is converted to cyclic and linear dimethylsiloxanes (D units):

$$(CH_3)_2SiCl_2 + H_2O \rightarrow \underset{\text{cyclic}}{[(CH_3)_2SiO]_n} + \underset{\text{linear}}{HO[CH_3)_2SiO]_mH} + HCl$$

Likewise, trimethylchlorosilane is converted to hexamethyldisiloxane, the source of chain-terminating M units:

$$(CH_3)SiCl + H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_3 + HCl$$

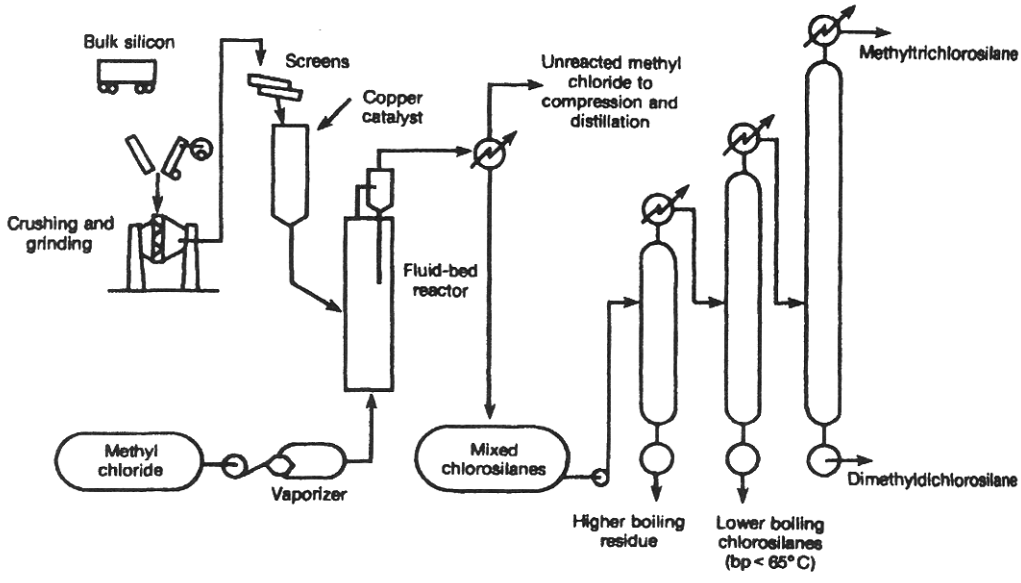

Figure 6 Conversion of bulk silicone.

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Table 3 Chlorosilane Properties

Compound	Boiling point (°C)	Density (g/cm^3)	Refractive index, n_D^{20}	Assay (%)
$(CH_3)SiCl_3$	66.4	1.273	1.4088	95–98
$(CH_3)2SiCl_2$	70.0	1.067	1.4023	99–99.4
$(CH_3)3SiCl$	57.9	0.854	1.3893	90–98
$(CH_3)SiH(Cl)_2$	41.0	1.110	1.3982	95–97
$(CH_3)2SiH(Cl)$	35.0	0.854	1.3820	

Siloxane polymer ($MD^{''}M$) is formed in the equilibration reaction:

$$[(CH_3)_2SiO]_n + HO[(CH_3)_2SiO]_mH + (CH_3)_3SiOSi(CH_3)_3 \xrightarrow{H^+ \text{ or } CH^-}$$
$$[(CH_3)_2SiO]_n + (CH_3)_3SiO{-}[{-}(CH_3)_2SiO{-}]_p = Si(CH_3)_3 + H_2O$$

The average chain length can be controlled reliably by choosing the ratio of D to M. (However, note that some cyclic siloxanes remain at equilibrium with the mix of polymer chains.) The equilibrated fluid is washed with water to kill residual active groups, then neutralized, dried, and devolatilized to yield the final silicone fluid product.

Commercial products can be pure or modified dimethyl silicone fluids. Fluids can be modified chemically by copolymerization with methyl alkyl, methyl phenyl, diphenyl, methyl trifluoropropyl, or other organofunctional oligomers. The addition of silica fillers to fluids gives greaselike silicone compounds, used for electrical insulation and waterproofing or as antifoam agents. The use of soap as a filler results in a lubricating grease.

IV. PROPERTIES AND PERFORMANCE

A. Structural Considerations

Silicones are used for lubrication in both critical (metal-to-metal) and noncritical applications, such as plastic-to-plastic. Critical lubrication conditions can be divided into three categories: hydrodynamic, boundary, and extreme pressure. These characteristics define the mechanisms whereby damage is prevented as one metal surface slides across another.

Early application testing soon made it clear that the most basic silicone, polydimethylsiloxane fluid (Fig. 7), in its unmodified and uncompounded state, lacks the ability to lubricate sliding metal-to-metal in any of the three categories outlined.

Dimethyl fluids as well as molecular modifications with phenyl were ideal in thermal and

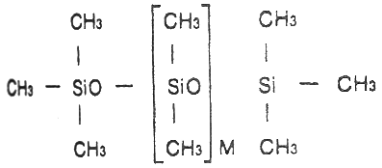

Figure 7 Structure of polymethylsiloxane.

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Table 4 Physiological Properties of Dimethyl Silicone Oils

Exposure	Effect
Skin	No reaction
Ingestion	LD_{50}, 15g/kg
Inhalation	No injuries known (low vapor pressure)
Eyes	Transient irritation
Patch testing	No skin irritation

oxidative stability. However, in viscosity and shear stability, they lacked the essential load-bearing characteristics necessary for critical lubricant use.

Molecular modifications utilizing phenyl alkyl, fluoro, nitrile, methyl alkyl, and chlorophenyl functionalities, and/or compounding with fillers such as soaps, graphite, treated or untreated silicas, molybdenum disulfide, polyethylenes, carbon blacks, clays, or combinations of the preceding are used to achieve the variety of lubrication properties necessary for effective critical lubrication.

Compounding lubricating fluids produces either greases or compounds. A grease is a "semi-structured lubricant that is utilized to lubricate or protect metal-to-metal contact surfaces" [13]. A compound is a fluid that has been thickened and stabilized to a greaselike consistency. Compounds are used for applications other than metal-to-metal.

B. Chemical and Related Properties

Generally speaking, silicones are chemically inert, self-extinguishing, resistant to oxidation and thermal attack, hydrolytically stable, nonstaining or noncorrosive, and, as a class of materials, very low in toxicity. The physiological properties of dimethyl silicone oils are presented in Table 4.

It is the Si—O linkage that contributes to the outstanding high temperature characteristics and general inertness of silicone fluids. The Si—O linkages are comparable to linkages found in similar high temperature materials (e.g., quartz, glass, sand). The carbon-hydrogen bonds of hydrocarbon fluids (Fig. 8) lack this relationship.

1. Chemical Inertness

Silicone fluids are inert to most common materials of construction. Generally, silicone polymers are unaffected by rubber, plastic, and most metals. However, the metals listed in Table 5 either cause or inhibit gelation of silicones.

Typically, water and ordinary aqueous solutions of inorganic acids or bases will not react

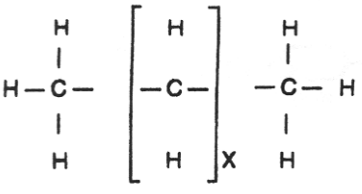

Figure 8 Hydrocarbon fluid structure.

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Table 5 Effect of Metals on Silicone at High Temperatures

Metal	Dimethyl (400°F)	Methyl phenyl (450°F)
Copper	Inhibits gelation[a]	None
Phosphor bronze	Inhibits gelation[a]	None
Lead	Inhibits gelation	Volatilization
Yellow brass	Causes gelation	None
Selenium	Causes gelation	Causes gelation
Tellurium	Causes gelation	Causes gelation

[a]Gelation is inhibited up to 400°F; at higher temperatures little effect is noted.
Source: Ref. 2.

with siloxanes intended for mechanical applications. However, strong acids or alkalies will cause molecular rearrangement and speed up gelation of silicone fluids under oxidative conditions.

2. Self-Extinguishing

Silicone polymers produce a white silica ash if burned and will eventually self-extinguish. See Section IV. C. 7 for additional information.

3. Oxidation Stability

In oxidative breakdown, oxygen reacts with the organic groups of the molecules, causing the fluids to lose volatiles and increase in viscosity until gelation occurs. The reaction is dependent on the temperature and supply of air present (Fig. 9).

At the point called the oxidation threshold temperature, significant amounts of oxidation by-products start to appear. Table 6 compares the oxidation thresholds of several silicone and organic fluids.

Although silicone lubricants are characterized as having a high oxidation threshold, they have poor tolerance for oxygen. Antioxidants are sometimes added to silicone lubricants to extend their lives at high temperature.

4. Thermal Stability

The best thermal stability for silicones is achieved in the absence of air or in an inert atmosphere such as nitrogen or carbon dioxide.

Under strictly thermal conditions where oxidation is not a factor, the bonds linking silicon and oxygen can be broken at very high temperatures. The result is the formation of lower molecular weight, volatile silicones at an activation temperature of approximately 316°C (600°F).

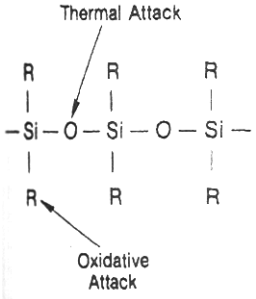

Figure 9 Thermal and oxidative attachment mechanisms.

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Table 6 Oxidation Threshold

Fluid	Oxidation threshold temperature, [°C (°F)]
Methyl phenyl siloxane (45 wt % MePh)	271 (520)
Chlorophenyl polysiloxane	221 (430)
Dimethyl polysiloxane	204 (400)
Dibasic acid ester	66 (150)
Petroleum oil	66 (150)

5. Hydrolytic Stability

When exposed to water at temperatures that will hydrolyze many other high temperature hydraulic fluids, silicone lubricating or hydraulic fluids will remain unaffected. Problems like gel precipitation and viscosity reduction will not be encountered.

6. Corrosion and Staining

Pure silicones contain no acid-producing chemicals to cause staining or corrosion, but chlorophenyl polysiloxanes have been known to produce negligible to slight staining. Since, however, structural surfaces containing copper have been known to discolor at 204°C (400°F) the use of pure copper with chlorophenyl polysiloxane is not recommended.

7. Effect on Plastics and Rubber

Although silicones are generally not affected by rubber or plastics, these materials can be affected by long immersion in silicone fluids. Very low molecular weight fluids (≤10 cSt) have been shown to have the most adverse effects, acting as solvents with plastics, and leaching out plasticizer in rubbers. Table 7 shows the effect on plastic after 30-day immersion in dimethyl and methyl phenyl silicones.

Plastics, coatings, and resins are generally not affected by silicone lubricants of moderate viscosity at ambient temperatures. Like many organic materials, however, silicone fluids may cause stress cracking polyethylene. Therefore, this plastic should be stress-relieved if it is to operate reliably in contact with silicone fluids for long periods of time. Cellulose acetate butyrate is stiffened and crazed by dimethyl fluids. Polyacetal (sold under the trade name Delrin) is stiffened and crazed by both dimethyl and methylphenyl fluids.

When silicone fluids are used to provide surface coatings on rubber to impart slip to rubber parts, no effect is noted. Rubber containing little or no plasticizer compatible with silicone fluids is unaffected. Table 8 lists the temperature ranges recommended for various rubber uses with silicone.

When silicones are used with these rubbers outside the recommended temperature range, the effect is usually a reduction of weight and volume and an increase in hardness due to leaching of the plasticizer.

C. Physical and Related Properties

Silicones' excellent viscosity–temperature characteristics, low temperature properties, and shear stability, along with their high compressibility, good radiation resistance, and low surface tension, are the physical properties that ensure their usefulness as lubricants.

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Table 7 Effect on Plastics After 30-Day Immersion in Silicone Fluid (SF)

Plastic[a,b]	Dimethyl SF96, at 350cSt	Phenyl containing SF
Nylon	No effect	No effect
Polystyrene	No effect	No effect
Methacrylics	No effect	No effect
Modified methacrylics	No effect	No effect
Polycarbonates (Lexan)	No effect	No effect
Phenolics	No effect	No effect
Cellulose acetate butyrate	Stiffened	No effect
Polyacetal (Delrin)	Stiffened and crazed	Stiffened and crazed
Polyethylene	Some stress cracking	Some stress cracking
Linear polyethylene	Some stress cracking	Some stress cracking
Linear polypropylene	Some stress cracking	Some stress cracking
Polyvinyl chloride	Shrinks and hardens	Shrinks and hardens
PTFE (Teflon)	No effect	No effect

[a]Linear polyethylene and linear polypropylene are not as susceptible to stress cracking or crazing as ordinary polyethylene.
[b]Teflon is a registered trademark of E. I. duPont de Nemours & Co., Inc.; Lexan is a registered trademark of General Electric Company; Delrin is a registered trademark of Dow Chemical Company.

1. Viscosity–Temperature Properties

Silicones experience a relatively small change in viscosity with regard to temperature. Other fluids (e.g., petroleum oils, dibasic acid esters) exhibit larger changes in viscosity with temperature than most silicones (Fig. 10).

The viscosity–temperature coefficient (VTC) is an indication of how much the viscosity changes with temperature. The lower the value, the less the viscosity changes with temperature. The relationship is expressed as follows:

$$\text{VTC} = 1 - \frac{\text{viscosity at 99°C (210°F)}}{\text{viscosity at 38°C (100°F)}}$$

Silicones generally have a VTC of only 0.6. This is different from organic fluids, which typically

Table 8 Rubber in Silicone Fluid Systems

Type	Product[a]	Recommended service temperature range (°F)
Chloroprene	Neoprene	−40 to 200
Isobutylene isoprene	Butyl	−40 to 200
Nitrile-butadiene	Nitrile Buna-N	−40 to 300
Fluororubber	Viton Fluorel	−20 to 450

[a]Neoprene and Viton are registered trademarks of E. I. duPont de Nemours & Company, Inc.; Fluorel is a registered trademark of Minnesota Mining & Manufacturing Company.

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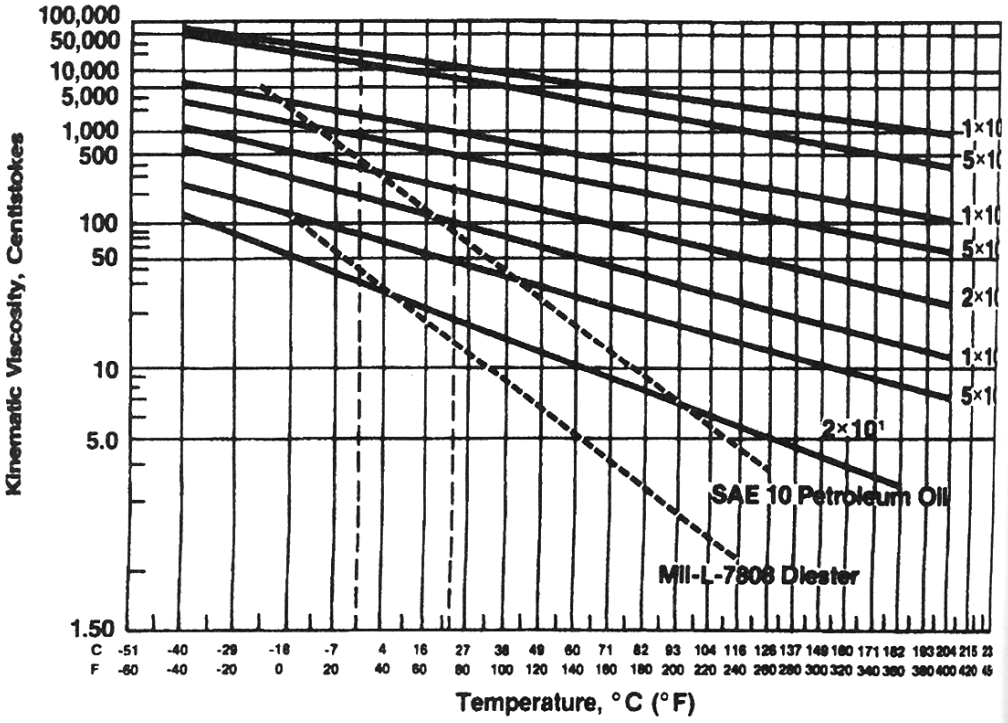

Figure 10 Viscosity–temperature relationship of dimethyl fluids (20–10,000 cSt at 25°C) versus selected hydrocarbon oils.

have a value of 0.8 or higher. Figure 10 shows viscosity–temperature relationships among various fluids.

2. Low Temperature Properties

Low-temperature fluidity is an important advantage held by silicones over conventional oils. It is measured by pour point: the temperature at which a fluid is so cold that it loses its ability to flow. Although analogous to the freezing point of a pure compound, the pour point of a polymeric fluid is not sharply defined and can vary with the test method. The most common method is ASTM D-97.

Basic dimethyl polysiloxanes above 50 cSt have characteristic pour points of −50 to −54°C (−58 to −65°F). By means of specially formulating fluids, pour points down to extremely low values can be achieved. Typically, branched siloxanes remain pourable at the extremely low temperature of −84°C (−120°F).

3. Shear Stability

Low molecular weight or low viscosity silicone fluids are essentially Newtonian in behavior. This means the measured viscosity does not change with different rates of shear. Dimethyl polysiloxanes of 40–1000 cSt at 25°C (77°F) are typical examples of this category.

Fluids with viscosities above 1000 cSt at 25°C (77°F) exhibit pseudoplastic flow. This means that there is deviation from linearity when the apparent viscosity is plotted against the

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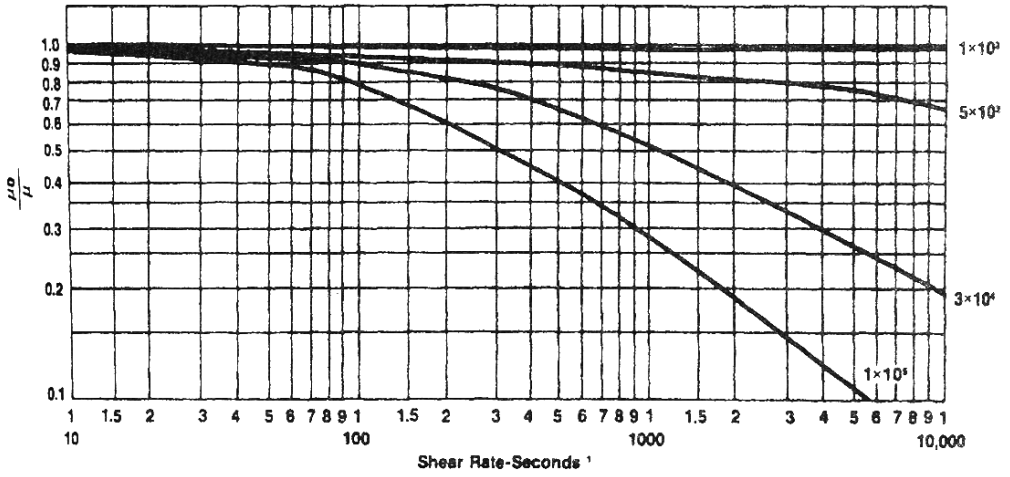

Figure 11 Transitory viscosity of dimethylsiloxanes (1000–100,000 cSt at 25°C) under shear conditions.

rate of shear. Further, as the viscosity increases, the deviation becomes more pronounced (Fig. 11).

Additionally, the loss of viscosity is much smaller that that of organic fluids, and silicone fluids will return to their original absolute viscosity as long as the temperature remains below 316°C (600°F).

Table 9 shows the stability of a methyl cholrophenyi siloxane in a pumping test. Compared with MIL-H-5606 in the same type of pump, the methyl cholrophenyi fluid was pumped hotter and longer, and the resulting viscosity change and pump wear were negligible.

4. Compressibility

All fluids show some tendency to decrease in volume when subjected to high pressures. Silicone fluids are considerably more compressible than natural oils like petroleum products.

It has been stated that a siloxane bond is like a ball and socket—free to move in any

Table 9 Shear Stability in Pumping Tests[a]

Fluid	Methyl chlorophenyl siloxane	MIL-H-5606
Pressure, psig	4000	4000
Temperature, °F	215	175
Test duration, h	1200	500
Recirculation, cycles	44,000	20,000
Flow rate during test	Constant	Dropped, > 8%
Fluid replaced	None	> 50% (leakage)
Pump wear	Nil	Serious
Viscosity change, cSt, at 38°C (100°F)	−3.5%	−25%

[a] Pump used: Lockheed MK 7 radial piston.

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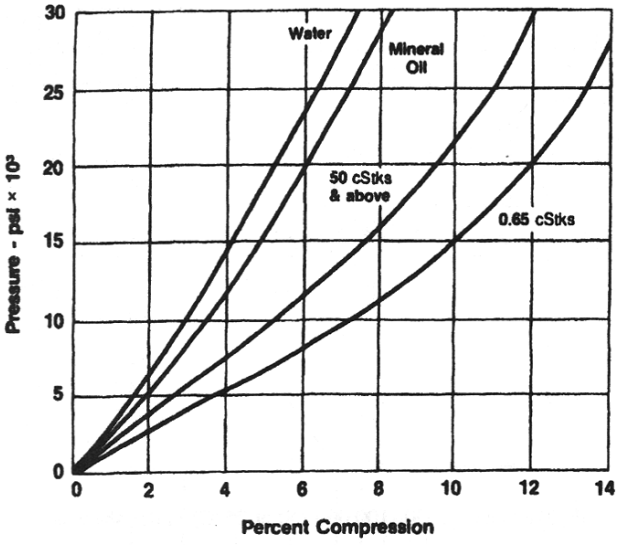

Figure 12 Compressibility of silicone fluids versus mineral oil and water.

direction. When a load is applied to the "chain," the linkage deflects, compressing the chain. The compression here is greater for siloxane because the spacing between the silicone and oxygen is greater than that of a hydrocarbon bond. Temperature has only a small effect over a range of −40 to 149°C (−40 to 300°F).

The low viscosity silicones have been found to be most compressible. For example, a dimethyl siloxane of 0.65 cSt was found to offer 17% volume reduction at 50,000 psi. However, the low volatility and effect on materials of construction make fluid of this viscosity inappropriate for many lubrication applications. A dimethyl siloxane of 1000 cSt was found to offer only a 15% decrease in volume reduction under a pressure of 50,000 psi.

Figure 12 and Table 10 provide pressure versus percent compressibility data for selected silicone fluids.

5. Radiation Resistance

It has been shown that radiation resistance is a function of aromatic content for both silicones and organic fluids. The dimethyl siloxanes contain no aromatic groups in their structure. Methyl and phenyl siloxanes and other aromatic siloxanes, therefore, demonstrate a much greater radiation resistance.

Table 10 Compressibility of Selected Silicone Fluids at Four Pressures

	Compressibility (%)			
Polydimethyl siloxane fluid	7100 psi	35,500 psi	284,000 psi	568,000 psi
100 cSt	4.5	12.7	28.6	34.0
1,000 cSt	4.6	12.7	28.2	33.5
12,500 cSt	4.5	12.5	28.1	33.5

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Dimethyl silicone fluids show relatively poor resistance to gamma radiation. Tests have shown that a dose of 1×10^7 roentgens will produce a large increase in the viscosity of dimethyl fluids. A dosage of 1×10^8 roentgens is usually sufficient to cause gelation. A methyl phenyl siloxane with 40–50 mol % phenyl would show minimum change at 1×10^8 roentgens. A methyl chlorophenyl siloxane of 8–13.5 mol % tetrachlorophenyl would demonstrate better resistance than a dimethyl siloxane, petroleum oil, dibasic acid ester, silicate, or disiloxane ester.

Theoretical treatment of the effects of radiation on silicone can be found in Refs. 20 and 21.

6. Surface Tension

Because their surface tension is usually low, silicone fluids are appropriate for applications calling for high surface activity and great spreading power.

Dimethyl silicones have the lowest surface tension values, and these are largely independent of viscosity [about 21 dyn/cm at 35°C (77°F) over a viscosity range of 20–100,000 cSt]. Methyl phenyl fluids have slightly higher surface tension values [about 24–25 dyne/cm at 25°C (77°F)], but these values are still much lower than those of organic materials.

The surface tension of organic fluids is typically in the range of 30–40 dyne/cm. The value of water at room temperature is about 72 dyne/cm.

7. Other: Flammability

Characteristic of silicones are high flash, fire, and autoignition temperatures. Conventional silicone fluids of 50 cSt or more in viscosity have flash points of 238–302°C (460–575°F) when measured by the conventional "closed-cup" method.

The fire points of silicones are significantly higher than their flash points. It has been estimated that their closed-cup fire points can be as much as 93°C (200°F) higher than their flash points. The difference between the flash and fire points accounts for the self-extinguishing characteristics of nonvolatile, high molecular weight silicone fluids. Conventional nonsilicone fluids frequently have flash and fire points within a few degrees of each other, reducing the likelihood that they will self-extinguish.

The autoignition temperatures for conventional silicones are estimated to be in the 438–460°C (820–860°F) range.

D. Performance Data

Typically, silicones operate at temperatures between −73 and 232°C (−100 to 450°F). Specially formulated silicones like the chlorophenylmethyl silicones have been known to operate at temperatures up to 315°C (600°F). Other modified silicones like the methyl alkyls cannot operate continuously above 350°F because of the limited oxidative stability inherent in the fluid.

In one of the most popular lubricating applications for high performance silicones (ballbearing lubrication), the concept of "speed factor" or DN values (bearing bore diameter in millimeters, times speed in rpm) is used to define the operating capability of silicone and other bearing lubricants. Silicone fluids used as bearing lubricants are recommended for use between 200,000 and 350,000 DN at light to medium loads. This recommendation is also true for most silicone greases that were designed primarily for antifriction bearings.

Silicone greases are known to provide extended bearing life over a wide operating temperature range. They are limited by the physical properties of the base silicone oil, in addition to the thickener chosen.

While the DN value defines the operating capability of lubricants, tests like the Shell four-ball wear test, the Falex test, and the Ryder gear test are widely accepted screening and perfor-

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mance tests for lubricants. Others, like the navy gear test, have poor reproducibility but were used in the past to characterize the performance of lubricants.

It has been demonstrated that chlorophenylmethyl siloxanes and methyl alkyl siloxanes, when properly formulated, compare favorably to traditional lubricants. Fluids or compounded methyl alkyl products have been known to perform even better than traditional lubricants in applications requiring aluminum-to-aluminum contact or lubrication of dissimilar metals. Conventional silicones compare poorly to traditional metal-to-metal lubricants in these tests.

Other specialty formulations like trifluropropyl methyl fluids or even silicone glycol fluids have improved lubricating properties under certain conditions. Often, however, physical properties or the inherent stability of the siloxane chain are compromised.

1. Four-Ball Wear Test

Performance under sliding contact is measured by the four-ball wear test. Table 11 compares typical wear scar data for a number of fluids in the temperature range of 25–75°C (77–167°F) in steel-to-steel applications. Methyl alkyl silicones are not included in the data in Table 11. However, in other studies, methyl alkyl fluids were compared to SAE 30, a traditional petroleum lubricant. The fluids were used to lubricate sliding aluminum S2 versus stationary tool steel with a load of 40 kg. The test temperature is 75°C (167°F) at speeds of 600 rpm. The methyl silyl siloxanes were scar-measured at only 0.55 mm, compared to a 0.70 mm scar for SAE 30 petroleum lubricant.

Table 11 Shell Four-Ball Wear Test: Comparison of Typical Data

Test fluid	Test conditions[a,b]	Wear scars (mm) at 10 kg	Wear scars (mm) at 50 kg
Petroleum base			
Mineral oil	167°F, 600 rpm	0.44	0.59
MIL-H-5606	Ambient, 600 rpm	0.30	0.55
SAE 10 engine oil	Ambient, 600 rpm	0.37	0.50
Dibastic acid esters			
Uncompounded			
Dibasic ester	Ambient, 600 rpm	0.52	0.79
MIL-6085A	Ambient, 600 rpm	0.60	0.85
MIL-L-7808	167°F, 600 rpm	0.22	0.40
Orthosilicate ester	167°F, 600 rpm	0.71	1.10
Phosphate ester	Ambient, 600 rpm	0.46	0.57
Polyphenyl ether	167°F, 600 rpm	0.56	1.25
Silicones			
Chlorophenylmethyl siloxane (8–13.5 mol % Cl_4Ph)	Ambient, 600 rpm	0.39	0.53
Dimethyl silicone	Ambient, 600 rpm	0.50	1.83
Dimethyl silicone	400°F, 1200 rpm	0.91	—
Methyl phenyl silicone (45 mol % MePh)	Ambient, 600 rpm	1.39	4.18
Chlorinated methyl phenyl silicone	Ambient, 600 rpm	0.80	2.32
Trifluoropropyl methyl silicone	400°F, 1200 rpm	0.54	—
Trifluoropropyl methyl-dimethyl copolymer	400°F, 1200 rpm	0.78	—

[a] Steel balls: AISI 52-100, time, 1 hour except 400°F/1200 rpm tested fluids, which are 2 hours.
[b] Tests performed at ambient temperature are initiated at approximately 25°C (77°F), but no effort at temperature control is attempted. Temperatures will rise 10–50°F (depending on the fluid); such data are roughly comparable to results of runs at 75°C (167°F).

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Table 12 Falex Test: Loads to Seizure

Dibasic acid ester	1150–2000 psi
Chlorophenylmethyl siloxane (8–13.5 mol % Cl_4Ph)	1100–1200 psi
Petroleum oil	600–900 psi
Methyl alkyl silicone	To 750 psi
Methyl phenyl silicone	50–100 psi
Dimethyl silicone	60–80 psi

2. Falex Test

Table 12 shows data on various lubricants that were subjected to the Falex test designed to measure the antiweld properties of lubricants and their resistance to wear under extreme pressure conditions.

3. Ryder Gear Test

The Ryder gear test (data generated using FS 791, method 6508) measures gross surface damage between case-hardened spur gears. Ratings are in terms of "scuff load," the load at which 22.5% of the gear tooth area is scored. Methyl phenyl silicones show some advantages in these tests. Performance is primarily dependent on the lubricant's "pressure–viscosity" properties: the greater the viscosity increase under pressure, the better the gear lubricant.Table13 presents data on selected fluids.

E. Applications

The applications of silicone fluids vary widely. They are used as base fluids for a variety of products such as emulsions, solutions, greases, and compounds. Although there are certain uses for silicone lubricating oils, more often the lubricant is in the form of a grease. Silicone fluids have found limited use as lubricants in applications calling for a material that can withstand high temperatures and moderately loaded conditions, but they are generally ineffective as lubricants for heavily loaded metal surfaces.

However, advances in technology have improved the load-carrying capabilities and lubricity of silicones; for example, fluorosilicone lubricants are effective in applications such as pumps and valves for fuel or solvent tanks in which the metal surface and the lubricant are exposed to hydrocarbon solvents.

Another drawback of silicone fluids—their adverse effect on the adhesion of postdecorative coatings such as paint—has also been addressed by technology. Methyl alkyl–substituted polysiloxanes possess unique properties that allow them to be used in areas where soldering and painting are being done.

A number of silicone fluids have been blended successfully with synthetic, organic fluids

Table 13 Ryder Gear Test: Scuff Loads

Methyl phenyl silicone	4000 psi
Dibasic acid ester	2800 psi
Versilube F-50®	2400 psi
Petroleum oil	1200 psi
Dimethyl silicone	1000 psi

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Table 14 Applications for Common Silicone Fluids

Silicone type	Properties	Applications
Dimethyl	Excellent viscosity–temperature characteristics, hydrolytic stability; reduces surface tension; imparts excellent slip to rubber and plastic; acts as a water repellent	Plastic bearings, sheeting, cutting tools, molded and extruded parts, sewing thread; base fluid for compounds, hydraulic fluids, damping fluids
Fluoro	Good lubrication and resistance to chemicals and solvents; extended bearing life; excellent high temperature properties; high load-carrying characteristics	Base fluid for greases, hydraulic fluids, bearings, chemical process compressors, vacuum pumps, other equipment used in chemical and corrosive environments
Methyl phenyl	Increased thermal stability; good high and low temperature stability; excellent radiation resistance; improved oxidation resistance	Base fluid for greases (maintenance and lube for life applications); imparts slip to rubber and plastic, hydraulic fluid, thread, and fiber
Methyl alkyl	Develops thick films under dynamic conditions; most compatible with organic materials; does not contaminate surfaces to be painted	Base fluid for greases, difficult metal combinations, die casting, metalworking, cutting oils, penetrating oils
Chlorophenylmethyl	Greatly improved high temperature lubricity; chlorine provides chemical reactivity with metal necessary for effective boundary lubrication; improved pour point	Miniature bearings; base fluid for grease, bearings in high ambient temperature industries, clocks and timing devices, hydraulic systems, tape recorders, vacuum pumps

to combine the best performance qualities of each. An example that has been marketed successfully is a diester–polysiloxane blend based on lithium soap. This product provides enhanced lubricating properties and lower cost compared with the polysiloxane equivalent.

Silicone fluids are also used extensively as release agents in a variety of molding operations. They are desirable because of their resistance to high temperatures, smoking, and fuming; and the small amount of product needed offsets their higher price.

Other applications include personal care products, paper coatings, hydraulic fluids, damping fluids, and polishing fluids. Table 14 lists the various types of silicone fluid, their properties, and the applications in which they are used.

V. MANUFACTURE, MARKETING, AND ECONOMICS

There are seven fully integrated competitors in the global silicones market (Table 15). Although these producers vary widely in size, each has a fairly complete product line. There are also a large number of specialty finishing companies, which purchase siloxane intermediates and process them into different elastomers, coatings, greases, compounds, and adhesives.

Overall demand for silicone fluids in the United States, Europe, and Japan grew at a rate of 10–15% during the 1970s as market potential and value in a wide range of slowed, reflecting maturing applications and displacement by lower cost materials. During the same period, however, new, more complex organomodified silicone polymers were introduced, increasing the overall use of silicone fluids as lubricants. In addition, a host of specialty silicone elastomers,

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Table 15 Major Global Producers of Siloxane Fluids

Company	Manufacturing sites
North America	
Dow Corning Corporation (a joint venture of the Dow Chemical Company and Corning Glass Works)	Midland, Michigan Carrolton, Kentucky Waterford, New York
GE Silicones	Sistersville, West Virginia
Osi (a Witco Company subsidary)[a]	South Charleston, West Virginia
Europe	
Dow Corning Ltd.	Barry, Wales
Wacker-Chemie GmbH	Burghausen, Germany
Rhône-Poulenc Specialités Chemique SA	Saint-Fons, France
Bayer AG	Leverkusen, Germany
Japan	
Dow Corning Toray Silicones Co. Inc.	Ichihara, Chiba Prefecture
Toshiba Silicone Company (a joint venture between Toshiba Corp. and GE)	Oha, Gumma Prefecture Annaka, Gumma Prefecture
Shin-Etsu Chemical Company	Takefu, Fukui Prefecture Naoetsu, Niigata Prefecture

[a]No longer producing methyl chlorosilanes.

coatings, and adhesives is expected to drive growth through the 1990s and beyond, with an anticipated growth rate of 8–12% for the next few years.

Because the products are similar, there is generally strong price competition among manufacturers of basic silicone fluids. In the case of more complex, specialty fluids, however, the issue is not competition, but rather price sensitivity on the part of consumers. Because they cost more than competing organic chemicals, silicones are considered high-end products and are selected for applications demanding their unique properties. Successful marketing and sales of these silicone fluids focus on the products' special qualities or value-added economics. Within the past few years, an increasing share of silicone fluid production has been dedicated to specialty products. This trend drives new technology and product development.

The highly engineered nature of specialty silicone products demands an investment in technology. The high cost of this technology has led to different product marketing strategies among the producers. Some have bundled specialty silicone products with organic specialties and targeted them at specific lubricant markets. Others have consolidated, formed joint ventures, or sold their interests to competitors. However, all these approaches are based on bringing value to the customer in specialty products like specialty lubricants.

The silicone industry has experienced a major shift from growth within traditional geographic boundaries to a global marketing approach. Silicone producers seek to improve existing product lines, develop new products, and enter new markets.

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